# INTERRELATIONSHIPS BETWEEN COAL ANALYSIS, COAL CONVERSION AND COAL STRUCTURE

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Models for the average structure of a coal and for its chemistry both rely heavily on analyses that are subject to considerable errors. In addition to these analytical problems, it is often true that our notions concerning the "reasonableness" of a chemical reaction of a coal are influenced by our conception of what an average structure for that coal looks like. This picture of an average structure for a coal was in turn probably influenced by analytical results obtained for extracts and/or products of "mild" reaction conditions. These two factors -- the weakness of analytical techniques for solid coal, and the somewhat circular dependence of our concept of coal structure on coal chemistry -- present problems for studies of both coal structure and coal chemistry. The development of improved analytical techniques for solid coal as well as for characterization of coal chemistry, is very important to any improvement in our real knowledge of coal and its significant fuel- processing chemistry. Several projects at PETC have focused on improvement of our ability to characterize solid coal and its fundamental chemistry during direct liquefaction.

A large number of average structural models for specific coals have been published, and many describe in some detail how the structure was derived (1). The input data include elemental analyses (C,H,N,O,S), possibly an aromaticity from 13C NMR, and often some characterization data on extracts or mild-reaction products. It is emphasized by everyone who publishes an average structure that the structure is only a statistical entity and is not meant to represent the organic structure of a coal on a molecular scale. Although we are repeatedly cautioned, it is easy to let our thought processes concerning chemistry be influenced by such attractive (seductive) visual representations. It is worthwhile to look at the potential errors in the data used for generation of an average structure or for describing a chemical reaction of coal.

Determination of the elemental composition of coal is routinely accepted as a starting point for describing a coal's structure; however, the distinction between organic and inorganic forms can lead to problems. The recent paper by Ehmann et al. (2) reviews the well-documented problems associated with determination of organic oxygen in coals. This problem is in part related to the lack of an accurate analytical method for the determination of water. Because of the sequence of steps in a total elemental analysis of coal, residual water remaining after drying translates directly into errors in both organic oxygen and organic hydrogen. Similarly, the accepted method for determination of organic sulfur is by difference (3) and thus contains a significant coal-specific uncertainty related to the dispersion of pyritic sulfur in the coal. The rather bleak picture is that there is significant uncertainty in three of the five major elements in the organic structure of coal.

The composition of coal extracts is a very important input to construction of coal models; however, this extract rarely appears explicitly in average structural models that focus on representing the insoluble matrix of a coal structure. The amount of extractable material that is truly soluble, so that it can be analyzed by modern techniques, is usually rather small (5-15%). Inference of an overall coal structure from the 5% of its composition that can be analyzed is always fraught with difficulties. The yield of extract can be raised significantly by a variety of thermal and chemical means; however, these extracts may be criticized as being too substantially transformed to be meaningful for coal structural studies. How would a reviewing organic chemist react if the identification of an organic solid was accomplished by analyzing the sample as a THF extract after heating to 300°C with 10% water and 15% added mineral matter?

Bulk spectroscopic analyses of coal that are capable of yielding direct structural information on the solid are infrared (IR) and nuclear magnetic resonance (NMR). Infrared spectroscopy is always capable of yielding qualitative information, but quantitation has proven elusive. The solid-state CP$^{13}$C NMR spectra of coal can provide very useful structural information; however the question of what fraction of the total carbon is being observed is still being debated (4). If the $^{13}$C aromaticity is determined on a nonrepresentative fraction of the total carbon, our picture of the average structure of a coal may be seriously in error.
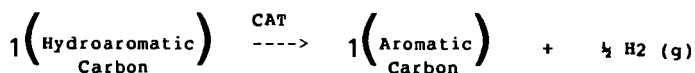
Investigation of chemical reactions involving coal is rendered very uncertain by our problems in analyzing the coal itself. It is difficult to describe the chemistry of an organic reaction when the nature of the starting material is uncertain. An improved understanding of the fundamental chemistry of direct liquefaction is an ongoing area of interest at PETC. This goal requires development of analytical techniques appropriate to the coal liquefaction system. One approach has been application of CP-MAS-$^{13}$C NMR techniques for measurement of net hydrogenation. By combining this measurement with material balance information, it is possible _in principle_ to determine the relative amounts of hydrogen consumed in hydrogenation, bond cleavage, and heteroatom removal.

The analysis of a variety of liquefaction systems using this hydrogen utilization approach has led to several conclusions: (1) under conventional liquefaction conditions, the net hydrogen consumed in hydrogenation of aromatic components is often small, (2) significant changes in "conversion" measured by solvent solubility can be accomplished with virtually no _net_ hydrogen chemistry, and (3) analytical methods for analysis of slurries of coal and vehicle oil are a major limitation to the improvement of our understanding of coal conversion chemistry. A typical hydrogen utilization profile for a coal conversion experiment conducted at 380°C is shown in Table 1.

The conversion of coal to THF solubles was in excess of 80% in this experiment. Although the experiment indicates an >80% "conversion", all of the numbers in Table 1 may be nonsignificant because of experimental error. A major potential contributor to the experimental error in both heteroatom removal and total hydrogen consumption is the inability to accurately determine water in coal. If 1 wt % molecular water exists in the "dry coal"

the analytical method conventionally used for direct oxygen and hydrogen determinations translates this water content into an error of -2 H/ 100C in the coal and would also result in a significant overestimation of the amount of organic oxygen in the slurry. This sensitivity of organic hydrogen and organic oxygen to the accuracy of the water determination indicated to us a need for improved confidence in the coal moisture analysis. A recently completed study of the water content of a variety of coal samples, both from the Argonne sample bank and from coals typically used for liquefaction research, indicates that the problem may be significant, especially for air-dried (or mildly air oxidized) samples (5). This study used an isotope exchange procedure that is capable of determining water that is not volatile under conditions of the ASTM procedure. The method does not require removal of the water from the coal to obtain an analysis. It is hoped that this method will provide a more accurate evaluation of the water content of a coal, which in turn will improve the accuracy of organic oxygen and hydrogen determinations.

Another significant uncertainty in discussions of coal chemistry is the measurement of the hydrogen within the slurry that is available in hydro-aromatic structures. Such structures as the hydropyrenes have repeatedly been shown to be very effective in enhancing coal conversion. However, the content of such materials in complex heavy recycle vehicles, not to mention coal, is not easily determined. The content of multi-ring hydroaromatics in a coal structure is very important in establishing the amount of <u>internal</u> hydrogen readily available for participation in thermolytic reactions. Catalytic dehydrogenation of coal and vehicle has been used as a measure of this available hydrogen. We have attempted to use this technique coupled with NMR measurement of the aromaticity change on dehydrogenation to better understand the source of the hydrogen in such experiments. Conversion of a hydroaromatic to an aromatic with $H_2$ generation should conform to the following stoichiometry:

$$1 \left( \begin{array}{c} \text{Hydroaromatic} \\ \text{Carbon} \end{array} \right) \xrightarrow{\text{CAT}} 1 \left( \begin{array}{c} \text{Aromatic} \\ \text{Carbon} \end{array} \right) + \tfrac{1}{2} H2 \, (g)$$

Thus it should be possible to plot change in moles of aromatic carbon versus moles of hydrogen gas produced and obtain a slope of 2 (moles of carbon aromatized per mole $H_2$ produced). An example of such a system, the Pd catalyzed dehydrogenation of the bitumen gilsonite, is shown in Figure 1. Gilsonite was chosen because of its apparent high hydroaromatic content and its complex composition. The slope indicated in Figure 1 is near enough to the theoretical value for classical hydroaromatic dehydrogenation to conclude that the approach may be workable. This very simple analysis is applicable to complex systems and has potential for providing quantitative information relevant to coal conversion chemistry. If condensation of aromatics is the dominant source of the hydrogen gas generated, then a slope near zero might be expected because condensation should not affect the carbon aromaticity, $f_a$. If the hydrogen produced from hydroaromatic dehydrogenation is subsequently consumed by some unspecified bond cleavage chemistry within the liquefaction system, a slope greater than two would be expected. This technique has some promise for investigating internal redistribution of hydrogen in coal- vehicle slurries at mild temperatures.

Another example of a well-accepted concept in coal chemistry that is difficult to study directly is the role of free radicals in the thermal chemistry of coal. The existence of a huge reservoir ($\sim 10^{19}$ spins/g) of stable radicals in coal itself complicates the direct observation of the effects of the incremental transient of thermolytically produced radicals via ESR[6]. An alternative method for observing the radical involvement in complex systems is to introduce into the system a nonintrusive chemical probe molecule sensitive to the presence of radicals. This approach attempts to circumvent our inability to directly monitor the formation and destruction of reactive free-radical species in coal with any reliability. The hope is that the appropriate probe will be selectively sensitive to the population of coal radicals that are directly involved in conversion. Recent work at PETC has used the equilibration of cis- and trans-decalin as a probe of the time-averaged steady-state concentration of radicals in complex coal liquefaction systems. A greater steady-state concentration of radicals results in a more rapid conversion of pure cis-decalin to the equilibrium mixture of cis and trans isomers. In this chemical-probe approach, only a small amount of a pure compound is added to the liquefaction feedstock. Because the chemistry of complex liquefaction systems is not likely to be perturbed by a small amount of additive, the chemical probe method has the potential to yield more relevant information than that from investigation of reactions in which a model compound is the sole or the predominant reactant. The decalin isomerization probe has been used to determine the steady-state concentration of free radicals in coal liquefaction using heavy petroleum resid as vehicle.

## Conclusions

Studies of the net chemistry of direct liquefaction have focused attention on a number of analytical deficiencies that limit our confidence in describing coal chemistry and/or coal structure. The most obvious analytical limitations are the accuracy of the $^{13}C$ $f_a$ value, which allows us to quantitatively assess the hydrogenation of aromatics, and the accuracy of the water determination in coal, which determines the accuracy of subsequent measurement of organic oxygen and hydrogen. These concerns are, of course, not new, but it is important that they be kept firmly in mind so that research aimed at resolving our analytical deficiencies can go on simultaneously with our investigations of the relevant chemistry of liquefaction and the structure of coal.

## References

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Table 1.

|                            | Hydrogens per 100 Carbons of Slurry |
| -------------------------- | :---: |
| Hydrogenation              | 1 |
| Heteroatom Removal         | 1 |
| Gas Production             | 0 |
| Matrix Bond Cleavage       | 2 |
| Total Hydrogen Consumption | 4 |

Conditions:     Feed = Illinois No. 6 coal (4g) + SRC II HD (7g)
                Temperature = 380°C
                Reaction Time = 20 minutes
                Catalyst = Molybdenum (as ammonium heptamolybdate), 0.006g
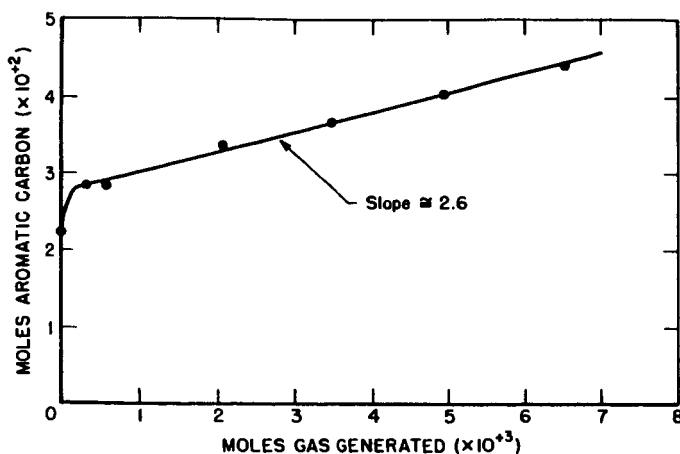                Gas = $H_2$, 2000 psi



Figure 1.   Relationship between change in aromaticity and gas generation on catalytic "Dehydrogenation" of gilsonite.